EQUATION OF STATE FOR A HIGH-DENSITY GLASS

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Abstract. Properties of relevance for the equation of state for a high-density glass are discussed. We review the effects of failure waves, comminuted phase, and compaction on the validity of the Mie-Grüneisen EOS. The specific heat and the Grüneisen parameter at standard conditions for a $\rho_0 = 5.085$ g/cm^3 glass ("Glass A") is then estimated to be 522 mJ/g/K and $0.1 - 0.3$, respectively. The latter value is substantially smaller than the value of 2.1751 given in the SESAME tables for a high-density glass with $\rho_0 = 5.46$ g/cm^3 [1]. The present unusual value of the Grüneisen parameter is confirmed from the volume dependence determined from fitting the Mie-Grüneisen EOS to shock data in Ref. [2].

INTRODUCTION

Brittle materials can exhibit failure waves. In glasses this phenomena is well studied; failure waves are found to exist in high- and low-density glasses. For example, the Hugoniot Elastic Limit (HEL) for DEDF glass ($\rho_0 = 5.18$ g/cm^3) is 4.3 GPa [3]. A slower failure wave is present for peak stresses from below the HEL to about 2 times the HEL. Thus, for certain peak states there is a complicated 3-wave structure with the elastic, shock and failure waves (there is evidence, though, that the failure wave is actually a diffusive process [4]). The Hugoniot relations have been shown to hold, to a good approximation, between the intact material and the comminuted material across the failure wave [3]. I also note that the failure wave not is due to tensile stress.

There are several studies of densification of silica glass [5] but not leaded glass. Silica has an open structure while high-density glasses with high lead content are considered "filled" materials and should not exhibit the large densification seen in silica. Note, however, in Fig. 1 that even though silica and low-density Pyrex glass exhibit a high degree of compaction, there also is noticeable compaction in the high-density glasses. I will discuss this issue further below in the context of composition. Note that the compaction in excess of comminution in the failure wave probably is due to a structural phase transition (e. g. Ref. [5]) in the grains of the comminuted material. Owing to its higher density the Mie-Grüneisen EOS should be valid for the comminuted glass.

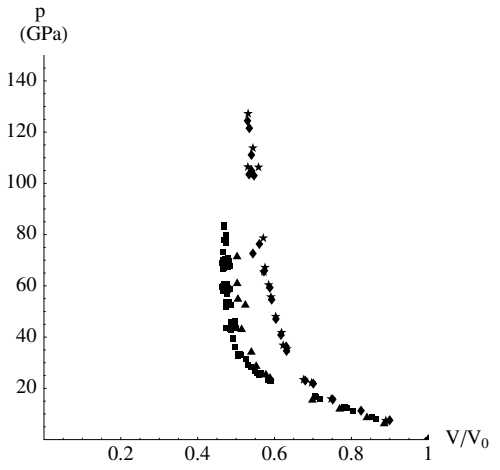

FIGURE 1. Hugoniots for 4 different glasses: Fused silica $\rho_0 = 2.204$ g/cm^3 (box), Pyrex $\rho_0 = 2.230$ g/cm^3 (triangle), $\rho_0 = 4.817$ g/cm^3 (diamond), and $\rho_0 = 5.085$ g/cm^3 (star). Data are from Ref. [2].

Because of the complicated behavior of glasses

I did not model the cold curve, $p_c(V)$, directly. Instead my analysis is based on available shock data, the Hugoniot relations, the Mie-Grüneisen EOS and two models relating the Grüneisen parameter to the derivatives of the cold curve. I will compare my result with data derived from modelling the cold curve [1].

ROUGH ESTIMATE OF THE GRÜNEISEN PARAMETER

With knowledge of the linear thermal expansion, α, the bulk speed of sound, c_0, and the specific heat, c_V, the thermodynamic Grüneisen parameter, Γ, can be deduced from the relation $\Gamma = 3\ \alpha\ c_0^2\ /c_V$.

Estimate of specific heat

The specific heat can be estimated, by the Dulong-Petit law, to be $3k_BN$, where k_B is the Boltzmann's constant and N is the number of atoms per unit mass. This value is only dependent on the composition of the glass (larger lead content gives smaller number of atoms per unit mass). Since we do not know the exact composition of Glass A it needs to be estimated.
Known compositions: (wt %)

- Fused silica, density 2.20 g/cm^3: SiO_2 (100).
- Glass ZF1, density 3.86 g/cm^3: SiO_2 (41.32), K_2O (7.00), As_2O_3 (0.50), PbO (51.18) [6].
- DEDF, density 5.18 g/cm^3: SiO_2 (27.4), K_2O (1.5), As_2O_3 (0.1), PbO (71.0) [3].

From the known compositions and densities above we can calculate the number of single atoms in a unit volume for each of these glasses. This number turns out to be almost the same regardless of composition. That is, the density difference between these three different glasses is mainly due to substitution of heavy PbO for light SiO_2 (trade 2 SiO_2 for 3 PbO). ZF1 and DEDF have exactly the same number of single atoms (within error-bars of the composition) while fused silica has 3% more atoms than these materials in the same volume. I assume the same total number of atoms in a volume in Glass A as in DEDF and ZF1. For simplicity I keep the K_2O and As_2O_3 content the same as in DEDF. The amount of PbO is, by far, the most important parameter for the density anyway. With these assumptions the composition is calculated to be:

- Glass A, density $\rho_0 = 5.085$ g/cm^3: SiO_2 (28.4), K_2O (1.5), As_2O_3 (0.1), PbO (70.0).

The number of atoms in a unit volume for the high-density glasses above is 0.1065 N_A cm^{-3} (N_A is Avogadro's constant), which gives a specific heat of 522 mJ/g/K for Glass A.

Note that in the classical limit the specific heat only depends on the number of atoms in a unit volume of the material and not on type of atoms. Since this number is nearly constant in glasses, the specific heat scales linearly with the inverse of the density (or linearly with the specific volume). The specific heat of the high-density glass in Ref. [1], with density 5.46 g/cm^3, can thus be estimated to 486 mJ/g/K. The value extracted from the data in Ref. [1] itself, by thermodynamic relations, is approximately 530 mJ/g/K, which shows that using the linearity for estimating the specific heat in glasses is sufficiently accurate for these purposes.

Estimating the Grüneisen parameter

Data for 31 different glasses are available in Ref. [7]. Where possible I have made consistency checks between these data and data from other sources and found no inconsistencies. Using the above estimate for the specific heat, the DEDF bulk speed of sound, 2.60 km/s, and the range of linear thermal expansions from the data sheet [7], the Grüneisen parameter is estimated to $\Gamma = 0.02 - 0.38$. The large uncertainty in this value stems from the thermal expansion, which varies substantially between glasses. The 3 leaded glasses available in the data sheet have thermal expansions of $83 - 95 \times 10^{-7}$ K^{-1}, implying a Grüneisen parameter in the upper end of the interval ($\Gamma = 0.32 - 0.37$). Fused silica, as an extreme, has only 5.5×10^{-7} K^{-1} ($\Gamma = 0.02$), while Pyrex has the more ordinary value of 32.5×10^{-7} K^{-1} ($\Gamma = 0.13$). We clearly see, however, that the Grüneisen parameter in glass is significantly lower than in more ordinary materials, where it ranges from 1.0 to 3.0.

This range of Grüneisen parameter values is about a factor of ten smaller than the value presented in Ref. [1] for a high-density glass with 5.46 g/cm^3. The speed of sound derived from the data in Ref. [1] is 2.8 km/s, not very different from the speed of sound we have used. The full difference is instead due to a linear thermal expansion value of 481×10^{-7} K^{-1}

derived from the data in Ref. [1] (giving a $\Gamma = 2.13$, the value given in Ref. [1] being 2.1751). I note that none of the 31 glasses in Ref. [7] has a thermal expansion coefficient even a quarter as large as this value.

FURTHER DISCUSSION ON COMPACTION

Contrary to some opinions, I believe a structural phase transition contributes to the compaction of the high-density glasses. All glasses with known composition mentioned above have nearly the same number of atoms in a unit volume, which indicates that there are no large structural differences between high and low-density glasses. However, Pb atoms in a condensed phase occupies larger volume than Si/O atoms (in the variety of silica phases the nearest neighbor (nn) distance is approximately 1.75 Å while the nn distance in a Pb crystal is 3.50 Å). This implies that the Hugoniot curve stiffens, governed by the inter-atomic forces in the compact phase, at a larger relative volume for the leaded glasses than for the low-density glasses. This is indeed seen in Fig. 1.

The statement that there is no compaction in high density glasses [3] is based on a comparison of measurements of the longitudinal strain in soda-lime glass, Ref. [8] Fig. 6, and DEDF, Ref. [9] Fig. 5. I do not find this conclusion well supported.

MIE-GRÜNEISEN EOS

We neglect any contribution from the electrons. Using the Mie-Grüneisen EOS, standard thermodynamics relations, a model (Slater-Landau (SL) or Dugdale-MacDonald (DM) [10]) for connecting the Grüneisen parameter to the derivatives of the cold curve, and the Hugoniot relations, $p_H(V)$ can be written as a function of only the cold curve $p_c(V)$ and the volume, V_{0c}, where $p_c(V_{0c}) = 0$. The procedure is outlined in Ref. [10], Chapter 13. By assuming that

$$p_c(V) = \sum_{i=1}^{6} a_i \left(\frac{V_{0c}}{V}\right)^{\frac{i}{3}+1}, \qquad (1)$$

and fitting the parameters a_i to the $p_H(V)$ data given in Ref. [2], the cold curve, and thereby the Mie-Grüneisen EOS, can be determined. In Fig. 2 the cold curve and the resulting Hugoniot are shown together with the data to which they were fitted. Note that we

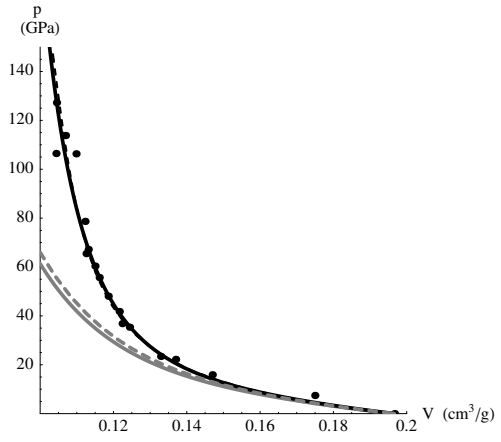

FIGURE 2. The resulting Hugoniot (black) and cold curve (gray) for Glass A from fitting to data in Ref. [2] (dots). The dashed cold curve results from the DM model and the solid from the SL model of the Grüneisen parameter. The dashed black line shows the Hugoniot derived from Eqn. 2.

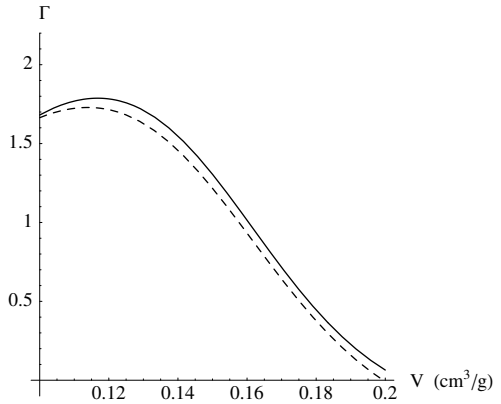

FIGURE 3. The Grüneisen parameter versus volume for Glass A. The solid curve corresponds to the SL model and the dashed to the DM model.

ignore the elastic region at low pressure. Fig. 3 shows the volume dependence of the Grüneisen parameter.

In the fitted curves, V_{0c} is chosen so that the bulk speed of sound is 2.6 km/s ($V_{0c} = 0.196300$ cm^3/g in the SL model, and 0.196600 cm^3/g in the DM model. The standard volume is $V_0 = 0.196657$ cm^3/g). The lower of the cold curves in Fig. 2 and the upper of the Grüneisen parameter curves in Fig. 3 are results

using the SL model (solid lines), the other two corresponding curves (dashed) result from the DM model. In this case the SL model seems to work best since it gives a more sensible value for the internal energy E_0, which is the temperature dependent specific heat integrated from 0 to standard temperature. In the SL we obtain a value of E_0 that corresponds to a mean specific heat of 364 mJ/g/K in the $0-300$ K range while the DM model gives a value of only 156 mJ/g/K.

Note that this derivation of the Grüneisen parameter is independent of the rough estimate of the value at standard conditions made above. This indicates that the present very low value is internally consistent.

The cold curve corresponding to the SL model (full gray line in Fig. 2), the model for the Grüneisen parameter I recomend in this case, is obtained from Eqn. 1 with fitting parameters (a_1, a_2, a_3, a_4, a_5, a_6)= (-2989.05, 8360.78, -7125.9, 313.609, 2149.33, -708.758). From this cold curve, the Mie-Grüneisen EOS and thereby the Hugoniot, $p_H(V)$ can be determined and a relation between the shock wave velocity, u_s, and particle velocity, u_p, in the shock wave can be calculated. I found that at least a third degree polynomial was needed to model this curve,

$$u_s = 2.64 + 0.51u_p + 0.42{u_p}^2 - 0.05{u_p}^3 , \quad (2)$$

as is seen in Fig. 4. The Hugoniot derived from Eqn. 2 is shown as a black dashed line in Fig. 2.

CONCLUSION

For a high-density glass with $\rho_0 = 5.085$ g/cm^3, the Grüneisen parameter has an unusual behavior and its value at standard conditions is in the range 0.1-0.3.

ACKNOWLEDGMENTS

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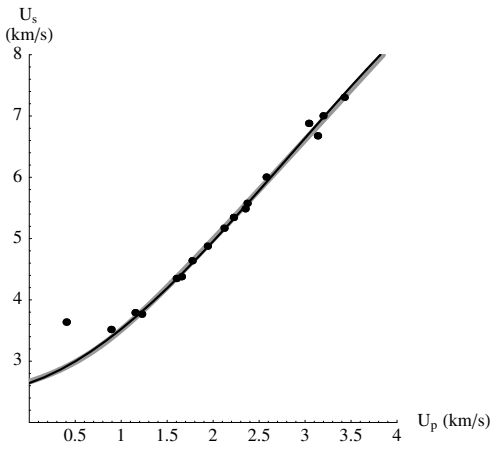

FIGURE 4. u_s vs. u_p for Glass A. The dots show data from Ref. [2]. The thin black line shows Eqn. 2, a fit to the thick gray line derived from the lower cold curve in Fig. 2.

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